Thermochimica Acta 630 (2016) 1–10

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Measurement and correlation of the solubility of (1-benzyl-1H-1,2,3-triazole-4-yl)methanol in water and alcohols at temperatures from 292.15 K to 310.15 K

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ARTICLE INFO

Article history:
Received 12 September 2015
Received in revised form 16 January 2016
Accepted 26 January 2016
Available online 22 February 2016

Keywords:
Solubility
Correlation
Thermodynamic property
(1-Benzyl-1H-1,2,3-triazole-4-yl)methanol

ABSTRACT

The solubilities of (1-benzyl-1H-1,2,3-triazole-4-yl)methanol (BTZM) in water, methanol, ethanol, *n*-propanol, isopropanol, and *n*-butanol were measured at temperatures ranging from 292.15 K to 310.15 K by a dynamic method under normal atmospheric pressure. The results showed that it increased with the increasing temperature and the order of solvents was: order: methanol > ethanol > *n*-propanol > *n*-butanol > isopropanol > water except three points. The solubility data were correlated with the Van't Hoff equation, modified Apelblat equation, and λh equation. The average relative deviations (ARD) were 1.87%, 1.53%, and 1.71%, and the root-mean-square-deviations (RMSD) were 2.37×10^{-2}, 1.51×10^{-2}, and 2.12×10^{-2}, respectively. It was found that the modified Apelblat equation gave the best correlation results. Furthermore, the dissolution enthalpy of BTZM was calculated by the modified Apelblat equation.

1. Introduction

1,2,3-triazole and its derivatives, five-membered nitrogen heterocyclic compounds, have been widely used in modern chemistry, agricultural, drug discovery, polymer materials, macromolecules, and functional materials [1–4]. (1-Benzyl-1H-1,2,3-triazole-4-yl) methanol (BTZM, $C_{10}H_{11}N_3O$, CAS RN 28798-81-4) is an important chemical intermediate and applied to synthesize triazole ethers [5], polynuclear azoles [6–8], and ligands [9,10] through replacing the alcoholic hydroxyl group with halogens and other nucleophilic reagents. Proton exchange membranes based on the 1H-1,2,3-triazole functional group showed good protogenic conductivity and thermal stability. Besides, the biological properties of BTZM have been attracted more attentions [11,12]. BTZM can be synthesized using benzyl halide, sodium azide, and propargyl alcohol as the raw materials. The solution crystallization is a key step in the manufacturing processes of BTZM. The accurate equilibrium solubility data of BTZM varying with temperature and solvent is overwhelming important to optimize crystallization processes and operation conditions. Many studies have focused on the synthesis of BTZM [13,14], but no report on the purification methods to get high purity product was found.

In this work, BTZM was synthesized and its structure was characterized by IR, and nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR). Its solubilities in water, methanol, ethanol, *n*-propanol, isopropanol, and *n*-butanol have been measured at temperatures ranging from 292.15 K to 310.15 K under normal atmospheric pressure using a dynamic method by a laser monitoring observation technique. The experimental solubility data were correlated with the Van't Hoff equation, modified Apelblat equation, and λh equation. Moreover, the dissolution enthalpy of BTZM in the above mentioned solvents was obtained by using the modified Apelblat equation.

2. Experimental

2.1. Materials

Benzyl chloride and propargyl alcohol were commercially available from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China) and Zhengzhou Xinshun Plating Co., (China), respectively. All of the solvents and sodium azide with analytical grade, purchased from Kermel Tianjin Chemical Co., were used to measure the solubility without further purification. The water used in the experiment was double-distilled water (conductivity < 4 μS cm^{-1}). Detailed information of the materials used in the work was listed in Table 1.

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http://dx.doi.org/10.1016/j.tca.2016.01.009
0040-6031/

Nomenclature

List of symbols

A	Parameter in Eq. (8)
a	Parameter in Eqs. (5), (7)
B	Parameter in Eq. (8)
b	Parameter in Eqs. (6), (7)
C	Parameter in Eq. (8)
c	Parameter in Eq. (3)–(6)
d	Parameter in Eq. (3)–(6)
h	Parameter in Eq. (9)
M_1	Molar mass of solute
M_2	Molar mass of solvent
m_1	Mass of solute
m_2	Mass of solute
N	Total number of experimental points
R	Gas constant (J mol^{-1} K^{-1})
T	Temperature (K)
T_m	Average melting point of BTZM (K)
x	Mole fraction solubility of solute
x^{exp}	The experimental mole fraction solubility of solute
x^{cal}	The calculated mole fraction solubility of solute

Greek letters

ΔH_d°	Standard dissolution enthalpy (J mol^{-1})
$\Delta_{fus}H^\circ$	Standard fusion enthalpy (J mol^{-1})
γ	Activity coefficient
λ	Parameter in Eq. (9)

2.2. Synthesis of BTZM

The synthesis mechanism of BTZM was shown in Fig. 1 and the specific synthetic method was described as follows:

First, benzyl chloride (42 mmol) was dissolved in the mixture of water (5 mL) and ethanol (40 mL), then NaN_3 (52 mmol) was added in three-necked flask with strong magnetic stirring. The formed solution was heated and refluxed for 8 h. After completion of the reaction, the reaction mixture was cooled. Afterwards water (100 mL) was added and extracted with diethyl ether (2 × 50 mL) three times, and the combined ether layer was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The colorless liquid benzyl azide (5.14 g, 92.1%) was obtained. The structure of benzyl chloride was characterized by IR (Fig. 2A) and benzyl azide was confirmed by IR (Fig. 2B), ^{1}H NMR (Fig. 3), and ^{13}C NMR (Fig. 4). ^{1}H NMR ($CDCl_3$, 400 MHz), δ(ppm): 7.50 ~ 7.46 (m, 2H), 7.45 ~ 7.39 (m, 5H), 4.39 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ(ppm): 54.83, 128.31, 128.38, 128.92, 135.50. Then, a solution of benzyl azide (25 mmol) and propargyl alcohol (30 mmol) in 30 mL tetrahydrofuran and a mixture of sodium ascorbate (2.5 mmol) and copper(II) sulfate pentahydrate (0.5 mmol) in 10 mL water were added in a 100 mL three-necked flask. The reaction mixture was heated and stirred at the reflux temperature for 20 h. After completion of the reaction, the reaction mixture was cooled to room temperature, then 100 mL water was added and extracted with dichloromethane three times, and the combined organic layer was dried with anhydrous sodium sulfate and desolventized. The yellowish green needles crystal BTZM (4.46 g, 96.0% purity by HPLC) was obtained and then recrystallized from ethanol three times to obtain the white needles crystal (more than 99.0% purity by HPLC).

2.3. Characterization of BTZM

The ^{1}H NMR spectra and ^{13}C NMR spectra were collected by a Bruker DPX-400 NMR spectrometer. IR spectra were recorded on the IR-200 spectrometer (Thermo Nicolet Corporation, America). The mass fraction purity of BTZM was identified by an Agilent-1100 high performance liquid chromatography (HPLC). The purity of solvents and raw materials used in this work were checked by the gas chromatograph (GC-7900. Techcomp(China) Ltd.). The melting point was determined by a WRS-1B digital melting point apparatus (Shanghai precision & scientific instrument Co., Ltd.). Fig. 2 presents the IR spectra of benzyl chloride (A), benzyl azide (B), and BTZM (C). For all the samples, the absorption band at approximately 3065 and 3032 cm^{-1} can be attributed to the stretching vibrations of =C—H on the benzene ring. The absorption bands appearing at 700 cm^{-1} in Fig. 2A is related to the stretching vibrations of C—Cl. Compared with Fig. 2A (benzyl chloride), the new

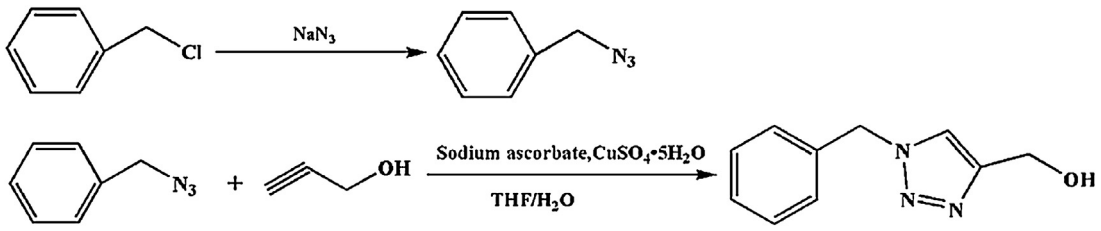

Fig. 1. Synthesis scheme of (1-benzyl-1H-1,2,3-triazole-4-yl) methanol (BTZM).

Table 1
The source and purity of the materials and the purification methods.

Material	Initial purity (mass fraction)	Purification method	Analysis method	Final purity (mass fraction)	Source
Benzyl chloride	0.990	Distillation	GC[a]	0.996	Sinopharm Chemical Co., Ltd.
Sodiumazide	0.990	–	–	–	Tianjin Kermel Chemical Co.
Propargyl alcohol	0.980	Distillation	GC	0.995	Zhengzhou Xinshun Plating Co.
Methanol	0.995	–	GC	–	Tianjin Kermel Chemical Co.
Ethanol	0.997	–	GC	–	Tianjin Kermel Chemical Co.
n-Propanol	0.998	–	GC	–	Tianjin Kermel Chemical Co.
Isopropanol	0.990	–	GC	–	Tianjin Kermel Chemical Co.
n-Butanol	0.995	–	GC	–	Tianjin Kermel Chemical Co.
BTZM	0.960	Recystallization	HPLC[b]	0.990	Synthesis

[a] Gas chromatograph.
[b] High performance liquid chromatography.